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Aerospace Research Center

MATERIALS DEPARTMENT

**Semiannual Technical Report
Contract Nonr 4644(00)**

Prepared for the
Scientific Officer
Physical Sciences Division
Office of Naval Research
Washington 25, D. C.

by

Dr. David Williams
Dr. Daniel Grafstein
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Sponsored by the
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Project Code No. 4730

31 August 1967

 **GENERAL
PRECISION
AEROSPACE**
Little Falls, New Jersey

RESEARCH CENTER • GENERAL PRECISION AEROSPACE

MATERIALS DEPARTMENT

LIQUID LASER PARAMETERS

Semiannual Technical Report
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Approved: Daniel Grafstein
Dr. Daniel Grafstein
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Manager, Materials Department

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FOREWORD

This is the Semiannual Technical Report on liquid laser parameters which covers research done under Contract Nonr 4644(00) between the Office of Naval Research and the General Precision Systems Inc., Kearfott Group - Aerospace Research Center, Little Falls, New Jersey. This report covers research performed during the period 1 February 1967 through 31 July 1967.

The authors of this report are Drs. David L. Williams and Daniel Grafstein. Dr. Irving Rowe of the Office of Naval Research, New York, has acted as Project Scientist. The authors are indebted to Mr. Alfred Brauer and Mr. William Ehrhardt for experimental assistance, to Dr. Aryeh H. Samuel, and Dr. Norman Blumenthal for many helpful discussions.

ABSTRACT

The results of a series of phosphorescence lifetime and intensity measurements on rare-earth coordination compounds are given and discussed. Enhanced phosphorescence has been observed in scrupulously anhydrous systems and the means of preparing such salts is described. The role of ligand vibrations in influencing nonradiative decay from excited levels is analyzed. Experiments with europium(III) in selenium oxychloride have lead to a hypothesis that it is critical to enhance nonradiative decay from excited levels to the emitting level. The need and means for improving the lifetime-measuring apparatus is presented along with planned modifications of the spectrophotofluorometer to allow measurements in the infrared region of the spectrum. Photochemical transformations in a particular europium(III) complex are noted.

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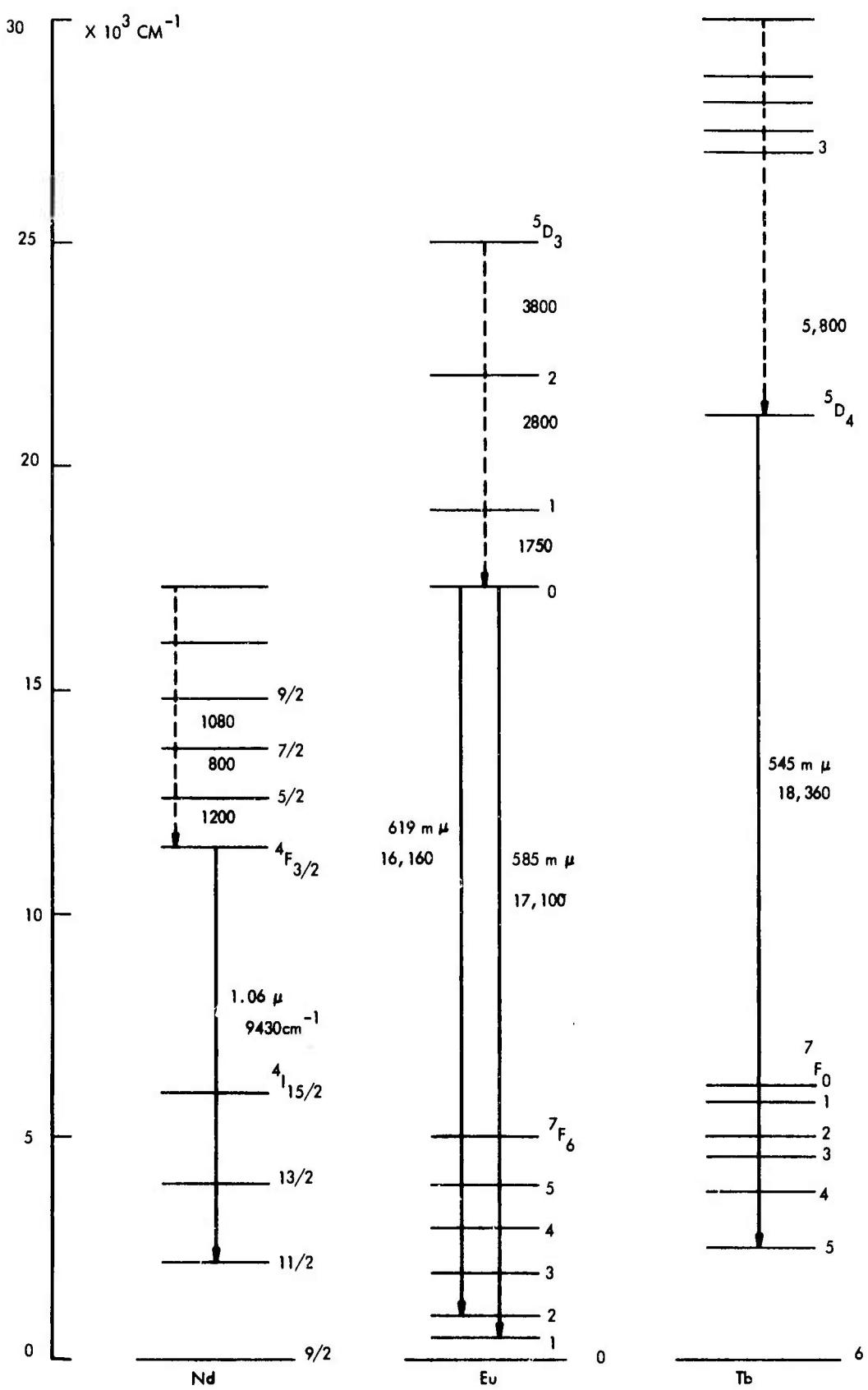
1. INTRODUCTION

This is the sixth semiannual report on the investigation of factors that influence the phosphorescence characteristics of rare-earth complexes in solution and covers the research performed during the period 1 February 1967 through 31 July 1967. This report is mainly concerned with the correlation of results derived from phosphorescence lifetime and intensity studies with the known chemical environment of the rare-earth ion.

In the last semiannual report, some of the theoretical aspects of energy-transfer mechanisms were discussed and the importance of nonradiative transitions were noted. Up to this time, the commonly accepted approach to enhancing phosphorescence of rare-earth ions has been to minimize nonradiative decay from the emitting level by utilizing ligands that have the lowest possible vibrational frequencies. Most of the basis for this concept has resulted from comparative studies of deuterated and non-deuterated ligands in europium(III) complexes.⁽¹⁻⁵⁾ The C-H stretching frequency is 3600 cm⁻¹ and the O-D frequency is 2700 cm⁻¹. As an example of the effect of deuterium substitution, EuCl₃ in D₂O has a reported phosphorescence intensity nineteen times stronger than the same salt in H₂O.⁽²⁾ However, the exact mechanism by which non-radiative decay is influenced by particular vibrational modes is poorly understood. Since a large portion of this research has involved europium(III) complexes, let us use the europium ion as an illustration.

In solution, the europium(III) phosphorescence is primarily two bands at about 585 and 619 m μ as indicated by the unbroken lines in the energy-level diagram of Figure 1. The strongest absorption is centered at 395 m μ and corresponds to an excitation to the ⁵D₃ level. The 585 and 619 m μ bands both originate from the ⁵D₀ level, and therefore the energy must cascade nonradiatively from the ⁵D₃ to the

* - References are given at the end of this report.



ENERGY-LEVEL DIAGRAM FOR TRIVALENT RARE-EARTH IONS
FIGURE 1

5D_0 level, probably in incremental steps by way of the 5D_2 and 5D_1 levels. There is nonradiative as well as radiative decay from the 5D_0 level, and also a significant amount of nonradiative loss from the 5D_3 , 5D_2 , and 5D_1 levels to ground. (6-7) Minimization of these nonradiative losses to the ground level is one obvious method to enhance phosphorescence. Though the various deuterium-substitution experiments have cast some light on the problem, there is still a great deal which is not understood about these systems.

Heller has shown that high-energy hydrogen-atom vibrations, especially O-H stretching vibrations, are strong phosphorescence quenchers,⁽⁵⁾ but they apparently affect the nonradiative decay only from the 5D_0 level and not the other levels, something which has also been confirmed in this laboratory^(3,4,6,7). A similar situation is present in terbium (III) systems where deuterium substitution affects nonradiative decay from the 5D_4 emitting level but not from higher levels⁽⁷⁾. We have studied deuterium effects in methanol systems and concluded that only vibrations of bonds adjacent to the atom directly coordinated to the rare-earth have any significant influence⁽¹⁰⁾.

The mechanism of nonradiative transfer of energy through vibrational modes is complex. According to Robinson,⁽⁸⁾ the rates of nonradiative transitions depend mainly on the magnitude of vibrational overlap integrals between initial and directly coupled final states of a system. In other words, the smaller the vibrational quantum number needed to approximate a given electronic energy gap, the greater will be the rates of nonradiative transitions. Presumably then, to reduce nonradiative decay, systems having low vibrational frequencies should be utilized. This concept lead Heller to experiment with heavy-atom inorganic solvents which resulted in the facile lasing of trivalent neodymium in selenium oxychloride.⁽⁹⁾

Our main mode of attack has been and is the study of means of influencing nonradiative decay and the attempt to gain further knowledge of energy-transfer mechanisms in rare earth complexes. As is indicated in the following paragraphs, our experimental results

cause us to postulate that the concept of employing ligands with low vibrational frequencies is probably only approximately valid and that there are other equally important factors to be considered.

Part of this consideration is due to our examination of the system europium(III) in selenium oxychloride. Following Heller's lead, europium(III) oxide was dissolved in a mixture of selenium oxychloride and stannic chloride to form a solution approximately 0.1M in europium(III). The stannic chloride acts as a Lewis acid and serves to increase the solubility of the europium salt. The phosphorescence of the resulting solution was measured and found to be weaker than for europium(III) salts in water (see Semiannual Report, August 1965 - January 1966), that is, there was almost complete quenching of the europium(III) radiative transitions. This is in contrast to the results found for neodymium(III) and indicates that simply a lower vibrational frequency of the complexing ligand is not automatically going to cause a phosphorescence-intensity enhancement.

To reach the emitting level of europium(III) or neodymium(III) it is first necessary for nonradiative decay to occur from the higher absorbing levels. For europium(III), this involves three transitions of 3800 cm^{-1} , 2800 cm^{-1} , and 1750 cm^{-1} ; for neodymium(III), there are five such transitions necessary, 1100 cm^{-1} , 1220 cm^{-1} , 1080 cm^{-1} , 800 cm^{-1} , and 1200 cm^{-1} (see Figure 1). These are nominal values and it must be realized that the transitions are actually broad bands, often 200 cm^{-1} wide. Selenium oxychloride has its maximum vibrational frequency at 955 cm^{-1} . In light of the dissimilar results for both europium(III) and neodymium(III) in selenium oxychloride, it is reasonable to postulate that enhancement of the nonradiative transitions from the absorbing to the emitting level is an important factor in phosphorescence radiation. The energy gaps above the emitting level in neodymium(III) match more closely the vibrational mode of selenium oxychloride than do the energy gaps above the emitting level of europium(III).

Further confirmation of the importance of the non-radiative transitions necessary to reach the emitting level arise from a study of the phosphorescence lifetimes of both EuCl_3 and TbCl_3 solvated with H_2O and D_2O ⁽⁴⁾. In these studies, there was a significant increase in the observed lifetimes when D_2O was substituted for H_2O .

However, for $\text{EuCl}_3 \cdot 6\text{D}_2\text{O}$, the phosphorescent decay was observed to be a two-step process, the $^5\text{D}_1 \rightarrow ^5\text{D}_0$ transition having a measurable lifetime. This transition has an energy of 1750 cm^{-1} . H_2O has two vibrational modes, 3600 cm^{-1} and 1620 cm^{-1} ; D_2O has vibrational modes of 2700 cm^{-1} and 1200 cm^{-1} . Thus, it would appear that H_2O is able to provide a better energy match for the 1750 cm^{-1} transition than is D_2O , and the phosphorescent decay for the H_2O solvated system is essential a one-step process.

Hypothesis of Phosphorescence Enhancement

There is no doubt that non-radiative decay from the emitting level is an important factor influencing phosphorescence and attempts must be made to minimize it. However, our analysis indicates that non-radiative decay to the emitting level is also of significant importance and that more emphasis should be placed upon this apparently neglected aspect of phosphorescence enhancement. Our hypothesis is that optimization of phosphorescence requires certain combinations of vibrational modes which will increase the rate of non-radiative decay to the emitting level while minimizing the rate of non-radiative decay from this same level. It should be emphasized that there is still a considerable amount of ambiguity concerning the exact mechanism of energy transfer and other factors which influence phosphorescence output. The selenium oxychloride results and the deuterium-substitution experiments discussed previously lead one to conclude that the problem is a complex one and much remains to be learned. It is certain that factors which influence the various selection rules governing both radiative and non-radiative transitions are of primary concern. The two methods generally employed to study such factors are the

phosphorescence lifetime and intensity measurements of various systems as a function of both the rare-earth ion and the ligand systems. In light of the discussion presented above, it would appear important to make such measurements as a function of absorbing level. In this manner, individual energy gaps down to the emitting level can be investigated, and the influence of each noted.

Phosphorescence Lifetime and Intensity Measurements

Phosphorescence studies have been made on a variety of complexes of europium (III) and terbium (III). The results are given in Table I. The following trends were noted: For relative phosphorescence intensities, $\text{DMAC} > \text{TEP} > \text{DMF}$ and $\text{NO}_3^- > \text{Cl}^-$; for lifetimes, $\text{TEP} > \text{DMAC} > \text{DMF}$ and $\text{Cl}^- > \text{NO}_3^-$. The highest vibrational frequency for each coordinated ligand is given below. These frequencies are shifted to lower energies from those of the pure solvents by 10 to 100 cm^{-1} .

DMAC (C=O)	1620 cm^{-1}
TEP (P=O)	1150 cm^{-1}
DMF (C=O)	1650 cm^{-1}

Accepting the simple concept that there exists a direct relationship between ligand vibrational frequency and quenching ability, one would expect TEP complexes, to yield the strongest phosphorescence intensity and DMAC and DMF complexes, to be weaker and almost identical to each other. This is not the case, and is only one more indication of the nature of the problem.

One possible explanation of the sequence found would be if coordination of the amides were through nitrogen instead of oxygen, either completely or partially. The C-N stretching frequency is on the order of 1100 cm^{-1} which puts it lower than the P=O stretching frequency of triethyl phosphate. Why then should DMF not be the same? DMF has a hydrogen atom adjacent to the C-N bond (and also the C=O bond) and as has been mentioned previously,

TABLE 1

Table of Phosphorescence Properties of Selected Complexes

	Intensity of $^5D_0 \rightarrow ^7F_2$ (619 m μ)	Intensity of $^5D_0 \rightarrow ^7F_1$ (595 m μ)	Lifetime in msec
Eu-N-H ₂ O	5.7	9.4	0.130
Eu-N-TEP	630	91	1.92
Eu-Cl-TEP	139	14.5	1.45
Eu-N-DMAC	794	88	1.23
Eu-Cl-DMAC	252	43	1.45
Eu-Cl-DMAC (anhydrous)	384	74	1.72
Eu-N-DMF	523	66	1.18
	Intensity of $^5D_4 \rightarrow ^7F_5$ (548 m μ)		Lifetime in msec
Tb-N-TEP	475		2.07
Tb-Cl-TEP	784		3.65
Tb-N-DMAC	784		1.57
Tb-Cl-DMAC	214		2.70

The intensity values are relative

N=nitrate; Cl=chloride; TEP=triethylphosphate; DMAC=dimethylacetamide; DMF=dimethylformamide

hydrogen atom vibrations appear to play an important role in phosphorescence quenching. Investigations of coordination number and site are being initiated by means of compositional and structural analysis, and these should greatly aid in understanding the operating mechanisms.

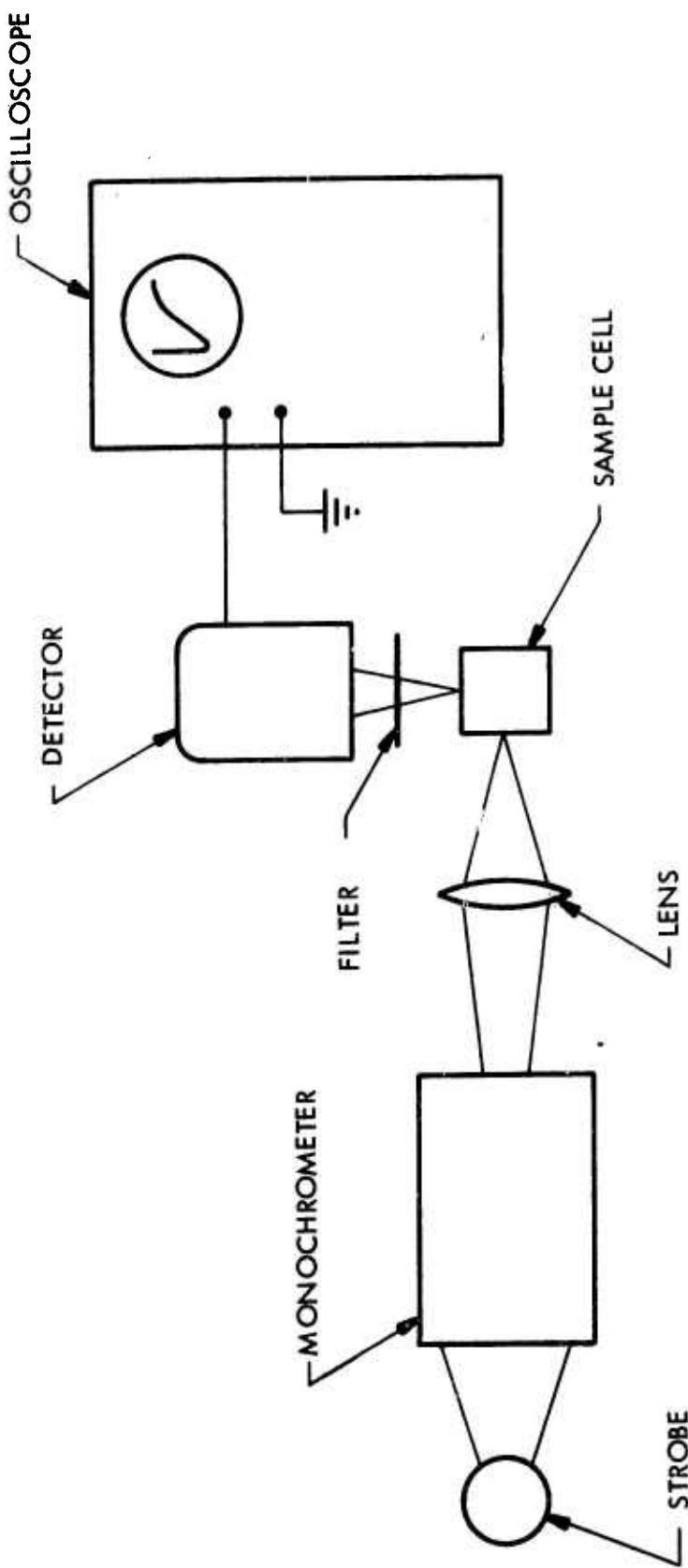
Lifetime Studies As A Function Of Absorbing Level

From the lifetime measurements made thus far, it has not been possible to distinguish definite differences in lifetimes as a function of excitation energy. Measurements of a number of europium (III) complexes were made at the excitation wavelengths of 395, 465, and $535 \text{ m } \mu$, and of terbium complexes at 375 and $475 \text{ m } \mu$. No differences in the lifetime values measured at these various wavelengths were larger than the experimental uncertainty. Thus, it can be stated that no lifetimes larger than about $70 \mu \text{ sec}$ are present in the levels above the emitting level in these systems. It is possible, however, that the uncertainties in the values are equal to or larger than the small expected differences. There is thus a need to make more accurate measurements.

Improvement Of Lifetime Apparatus

A diagram of the present instrumental arrangement used for conducting lifetime measurements is given in Figure 2. A polaroid picture is taken of the oscilloscope trace, and the time required for the intensity to decay to $1/e$ of its value is the defined lifetime.

Originally, a continuous source was employed in conjunction with a mechanical chopper. It was found that the transition time from full on to full off was of the same order of magnitude as the phosphorescence decay times. This means that the sample was being pumped while decaying, and the resulting curve was not exponential but a complicated superposition of different excitation and decay rates. To improve the situation, a high-



APPARATUS FOR LIFETIME DETERMINATION

FIGURE 2

power strobe was substituted for the continuous source and the mechanical chopper removed. The total decay time for the strobe is 1.5 msec., approximately half that of the mechanical chopper arrangement. However, even this is too long, and increased accuracy and flexibility would result from faster flash systems.

Another, and probably more important reason for going to a faster flash system involves studies of neodymium (III) complexes. Recently in this laboratory, laser action from certain solutions of neodymium chloride was observed. (11) There has thus developed an immediate need to examine the properties of neodymium (III) systems. Because the lifetimes of most neodymium (III) complexes are considerably shorter than those of europium (III) or terbium (III), being on the order of 100 to 200 μ sec⁹, it is important to use excitation pulses of very short duration. Flash tubes having pulse widths of 7 to 10 μ sec have been ordered along with their accompanying circuitry.

Modification Of The Spectrophotofluorometer

In order to study the phosphorescence intensity of neodymium (III) systems, it has been necessary to obtain a new grating for the Aminco-Bowman Spectrophotofluorometer. This grating is blazed at 700 $\text{m}\mu$ and allows measurements up to 1.20 μ (Nd(III) phosphoresces at 1.06 μ). The standard allows measurements only up to .8 μ . A new photodetector must also be used and presently experiments are being conducted with a 7102 photomultiplier. Some difficulties are being experienced, but it is expected that these will soon be overcome.

Non-Exponential Decay

Several of the oscilloscope traces of lifetime decay curves were plotted on semilog paper, and, if the decay curves were truly exponential, should have generated

straight lines. For both europium(III) and terbium(III) systems there was a significant curvature away from the time axis at long times. This type of behavior has been observed before, but no explanation has been suggested. Since for Tb-N-DMAC excited at 475 m μ there should be no two-step process, the non-exponentiality is probably instrumental in origin although it is possible that some unknown molecular process is occurring. The possibility that the non-exponentiality was the result of a non-linear response of the photomultiplier as a function of intensity was investigated. This was accomplished by varying the voltage impressed on the tube. The results were negative. Further studies of this problem are contemplated in order to determine whether or not the cause of this phenomenon is molecular in origin. The increased accuracy of the planned lifetime improvement should assist in this study.

Anhydrous Systems

It has been established (Semiannual Report, 1 August 1965 - 31 January 1966) that the presence of water tends to quench the phosphorescence of these rare-earth complexes. Thus, in order to increase phosphorescence and also eliminate water as a variable, it was decided to examine certain anhydrous systems.

A solution of anhydrous EuCl_3 was prepared with dimethylacetamide as solvent. Considerable difficulty was encountered in getting the anhydrous salt into solution. A saturated solution was reached at a concentration of 0.0155 M, the concentration being determined by atomic-emission spectroscopy. Phosphorescence studies of this solution as well as the corresponding hydrated one were made and the anhydrous system was found to have a lifetime of 1.72 msec, 1.25 times that for the hydrated system, and an intensity 1.5 times that for the hydrated system.

A sample of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in DMAC and the solution boiled down in a vacuum oven. The crystals were further dried under vacuum at room temperature and

and a portion dissolved in DMAC; a lifetime of 1.72 msec was found. This is the same as that for the solution mentioned above, which was made with anhydrous salt, and indicates that water of hydration may be easily eliminated negating the need to begin with expensive anhydrous salts. The results in general indicate that elimination of water does enhance the phosphorescence properties of these systems. To this end, we have acquired an inert-atmosphere box in which to prepare our samples under anhydrous conditions, and have set up a moisture-free distillation train for purifying solvents.

Energy Diagrams

In the last semiannual, it was shown that a measurement of the steady-state population of the emitting level of europium(III) under continuous irradiation would allow complete characterization of the europium(III) system and that an energy-transfer diagram could be constructed without reverting to drastic assumptions. It was proposed that such a measurement be made using electron paramagnetic resonance (EPR). Attempts were made to determine the EPR spectrum of a solution of europium(III) nitrate in triethyl phosphate through the courtesy of the New York University Physics Department. Considerable difficulty was encountered, and a well-defined spectrum could not be obtained. It is normally very difficult to achieve room-temperature EPR spectra of rare earths, especially in solution, and slight impurities are sufficient to prevent meaningful results. This work has been temporarily interrupted because of scheduling problems with the instrument. However, we plan to pursue this problem further as soon as possible.

Photodecomposition

During attempts to observe stimulated emission from several of the rare-earth systems, solutions of europium(III) chloride in dimethylacetamide, both hydrated and anhydrous, were flashed at 3000 volts. These solutions became discolored and lost all visible phosphorescence. Upon shaking the solutions in air, we observed that the

discoloration disappeared and the phosphorescence reappeared with its original intensity. The flashing obviously causes some sort of reversible photochemical reaction, the reversal most likely caused by oxygen. A solution of europium (III) nitrate in the same solvent failed to show similar behavior and no decomposition could be observed. The effect of oxygen would indicate a redox reaction, and since the phenomenon has been observed with the chloride derivative and not the nitrate, it is not unreasonable to postulate a reduction involving the breaking of a chlorine-europium bond forming an europium(III) derivative . Considerably more experimentation must be carried out to fully understand the processes occurring.

II. FUTURE PLANS

1. Homologous series of rare-earth complexes related to dimethylacetamide and other ligands will be prepared. Each complex will be analyzed spectroscopically and elementally. Special efforts will be initiated to determine the stereochemical structure of each complex.
2. Phosphorescence studies will be made on all complexes and the results correlated with the known chemical environment of the particular rare-earth ion.
3. A complete analysis of the various energy-transfer processes will be attempted. These studies will include absolute absorptions and emission measurements and an effort to determine the steady-state population of excited emitting levels with EPR.
4. A modification of the lifetime-measuring apparatus will be made to allow the determination of very short lifetimes as are found in neodymium(III) complexes. This will also considerably improve the accuracy of all measurements.
5. Modifications of the Aminco-Bowman Spectrophotofluorometer will be completed to allow determinations of neodymium(III) phosphorescence intensities.
6. Examine in detail the photochemical reaction and products observed in Eu-Cl-DMAC solutions.

REFERENCES

1. J. L. Kropp and M. W. Windsor, J. Chem. Phys. 39, 2769(1963).
2. J. L. Kropp and M. W. Windsor, J. Chem. Phys. 42, 1599(1965).
3. R. P. Borkowski, H. Forest, and D. Grafstein, J. Chem. Phys. 42, 2974(1965).
4. J. J. Freeman, G. A. Crosby, and K. E. Lawson, J. Mol. Spectry. 13, 399(1964).
5. A. Heller, J. Am. Chem. Soc. 88, 2058(1966).
6. W. R. Dawson and J. L. Kropp, J. Opt. Soc. Am. 55, 822(1965).
7. W. R. Dawson, J. L. Kropp, and M. W. Windsor, J. Chem. Phys. 45, 2410(1966).
8. G. W. Robinson, J. Mol. Spectry. 8, 66(1960).
9. A. Heller, Applied Phys. Letters, 9, 106(1966).
10. Unpublished results.
11. Contract DA-01-021-AMC-14727(Z).